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THE SOLUTION OF THE STEADY — STATE HEAT CONDUCTION EQUATION WITH CHEMICAL REACTION FOR THE HOLLOW CYLINDER

18 APRIL 1956

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

THE SOLUTION OF THE STEADY-STATE HEAT CONDUCTION EQUATION WITH CHEMICAL REACTION FOR THE HOLLOW CYLINDER

by

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ABSTRACT: The non-linear steady-state heat conduction equation which arises in the theory of thermal explosions, was solved by Frank-Kamenetzky for the case of the semi-infinite slab, and by Chambré for the solid cylinder and sphere geometries. Solutions for the case of the hollow cylinder are presented and it is shown that from these, the slab and solid cylinder solutions can be deduced as special cases. The design of large rocket grains, where self-heating may result in "spontaneous" ignition during manufacture or storage, is considered.

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These computations were performed under Task NOL-S6-2d-2-1-56, "Fundamentals of Solid Propellant Ignition and Burning". While present rocket grain webs are restricted to thicknesses which render spontaneous combustion of conventional propellants unlikely, the possibility must not be ignored. In particular, propellants with a low activation energy, low thermal conductivity, high density and high rate of decomposition are suspect. Within the assumptions made, the results of this study are believed to be accurate and are the responsibility of the author and the Fuels and Propellants Division of the Naval Ordnance Laboratory.

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THE SOLUTION OF THE STEADY-STATE HEAT CONDUCTION EQUATION WITH CHEMICAL REACTION FOR THE HOLLOW CYLINDER

INTRODUCTION

Let a combustible undergo an exothermic chemical reaction with heat loss to the walls of the containing vessel where this loss is assumed to take place via a conductive process inside the combustible volume. The criterion for thermal explosion is that the energy liberated during the reaction must be greater than that lost through the surfaces. The condition when the heat loss exactly compensates energy production in the combustible is described by the steady temperature state.

MATHEMATICAL MODEL

The steady state heat conduction equation can be written as

$$\lambda \nabla^2 T = -\rho Q Z \exp\left(-\frac{E}{RT}\right), \qquad (1)$$

where T is the combustible temperature, λ the thermal conductivity, ρ the density, Q the heat of reaction, Z the frequency factor, E the activation energy, R the gas constant, and ∇^2 the Laplacian operator. It is assumed that the reaction is unimolecular. The solution of Eq. (1) for the semi-infinite slab immersed in an isothermal bath at temperature, T_b, under the assumption* $T-T_b \ll T_b$ was first given by Frank-Kamenetzky (1). With the same assumption, Chambré (2) showed that the solution of Eq. (1) for solid cylindrical and spherical geometries can be obtained in terms of known functions.

Consider a hollow combustible cylinder of inner radius a and outer radius b whose isothermal surfaces are at temperatures T_a and T_b respectively. To solve Eq. (1) assume that $T-T_b \ll T_b$. Then to first order in $T-T_b/T_b$,

* The unpublished numerical integration of Eq. (1) for the slab and solid cylinder performed at the U. S. Naval Ordnance Laboratory has shown that this assumption is very good for the range $E/RT \geq 6$.

$$\frac{1}{T} = \frac{1}{T_b}\,\frac{1}{1+\frac{T-T_b}{T_b}} \simeq \frac{1}{T_b}\left(1-\frac{T-T_b}{T_b}\right) .$$

Setting $\theta = \frac{E}{RT_b^2}(T-T_b)$; $z = \frac{r}{b}$, (2)

Equation (1) becomes in cylindrical coordinates,

$$\frac{d^2\theta}{dz^2} + \frac{1}{z}\frac{d\theta}{dz} = -\delta \exp(\theta) \tag{3}$$

where r is the radial space coordinate and

$$\delta = \frac{\rho Q Z}{\lambda}\,\frac{E}{RT_b^2}\,b^2 \exp\left(-\frac{E}{RT_b}\right) . \tag{4}$$

Let $z = m$ when $r = a$. Equation (3) is to be solved subject to the boundary conditions

$$\theta = 0,\ z = 1 \qquad \text{at the outer surface}, \tag{5}$$

and at the inner surface,

$$\theta = \theta_m,\ z = m < 1 \tag{6}$$

Noting the method of solution by Chambré, the variables

$$\eta = z^2 \exp(\theta) \ ; \ \omega = z\frac{d\theta}{dz} , \tag{7}$$

are introduced and Equation (3) becomes

$$\frac{d\omega}{d\eta} = -\frac{\delta}{2+\omega} , \tag{8}$$

whose general integral is

$$\omega^2 + 4\omega + D = -2\delta\eta \tag{9}$$

The constant D (which was zero in Chambré's work) is in general different from zero. Rewriting Equation (9) in terms of the original variables, there results

$$\left(z\frac{d\theta}{dz}\right)^2 + 4z\frac{d\theta}{dz} + D = -2\delta z^2 \exp(\theta) , \tag{10}$$

which when compared with Equation (3), yields

$$z^2\frac{d^2\theta}{dz^2} - \frac{1}{2}\left(z\frac{d\theta}{dz}\right)^2 - z\frac{d\theta}{dz} - \frac{D}{2} = 0 . \tag{11}$$

The solution of this equation is

$$\theta = -2\ln\left(A z^{1+k} + B z^{1-k}\right) \tag{12}$$

where $k^2 = 1 - \frac{D}{4}$.

Boundary condition (5) gives

$$B = 1 - A \tag{13}$$

so that

$$\theta = -2\ln\left[A z^{1+k} + (1-A) z^{1-k}\right] \tag{14}$$

Boundary condition (6) is used to evaluate A, yielding

$$A = \frac{\gamma m^{-(1+k)} - m^{-2k}}{1 - m^{-2k}} \tag{15}$$

where $\gamma = \exp(-\frac{1}{2}\theta_m)$. Equation (12) still contains the parameter k whose relationship to δ will be found. Substituting Equation (14) into Equation (3) gives

$$\delta = 8k^2 A(1-A) . \tag{16}$$

Eliminating A between Equations (15) and (16) yields

$$\delta = 8k^2 \frac{(1-\gamma m^{k-1})(\gamma m^{k-1} - m^{2k})}{(1-m^{2k})^2} \tag{17}$$

which is the desired relationship between δ and k for given m and γ. From Equation (17) it can be shown that for given m and γ, δ has a maximum critical value, δ_c, for which the steady-state solution is still possible. When the value of δ as defined by Equation (4) exceeds δ_c, then thermal explosion will occur.

Introduce the new parameter

$$\alpha = m^{k} \tag{18}$$

so that Equation (17) becomes

$$\delta = 8\left(\frac{\ln \alpha}{\ln m}\right)^2 \frac{(m-\gamma\alpha)(\gamma-m\alpha)\alpha}{m^2(1-\alpha^2)^2} \tag{19}$$

Letting $d\delta/d\alpha = 0$, it is found that the root, α_c, of the equation

$$\frac{4\alpha}{\alpha^2-1} - \frac{1}{\alpha}\left(1+\frac{2}{\ln\alpha}\right) = \frac{\gamma}{\gamma\alpha-m} + \frac{m}{m\alpha-\gamma} \tag{20}$$

makes δ a maximum, δ_c, for given m and γ. From Equation (18) is obtained the critical value of k, k_c. Using Equations (14), (15), and (18), the critical temperature distribution, θ_c, is

$$\theta_c = 2\ln(1-\alpha_c^2) - 2\ln\left[\left(1-\frac{\gamma}{m}\alpha_c\right)z^{1+k_c} + \left(\frac{\gamma}{m}-\alpha_c\right)\alpha_c z^{1-k_c}\right]. \tag{21}$$

The critical temperature gradient is given by

$$\frac{d\theta_c}{dz} = -\frac{2}{z}\,\frac{(1+k_c)(m-\gamma\alpha_c)z^{2k_c} + (1-k_c)(\gamma-m\alpha_c)\alpha_c}{(m-\gamma\alpha_c)z^{2k_c} + (\gamma-m\alpha_c)\alpha_c}. \tag{22}$$

At the boundaries,

$$\left(\frac{d\theta_c}{dz}\right)_{z=m} = -\frac{2}{m}\left[1-\frac{k_c}{1-\alpha_c^2}\left(1-\frac{2m}{\gamma}\alpha_c+\alpha_c^2\right)\right]; \tag{23}$$

$$\left(\frac{d\theta_c}{dz}\right)_{z=1} = -2\left[1+\frac{k_c}{1-\alpha_c^2}\left(1-\frac{2\gamma}{m}\alpha_c+\alpha_c^2\right)\right]. \tag{24}$$

If f and h represent the energy flux and energy transfer rate per unit axial length, then

$$f = -\lambda \frac{dT}{dr} \ ; \ h = -2\pi\lambda r \frac{dT}{dr} . \tag{25}$$

Equation (25) c n be written as

$$F = -\frac{d\theta}{dz} \ ; \ H = -z\frac{d\theta}{dz} , \tag{26}$$

where

$$F = \frac{bEf}{\lambda R T_b^2} \ ; \ H = \frac{Eh}{2\pi\lambda R T_b^2} . \tag{27}$$

The position, z_o, of the maximum critical temperature, $\theta_{c,max}$, which occurs where $d\theta_c/dz = 0$, is

$$z_o = \left[\frac{k_c - 1}{k_c + 1} \ \frac{(\gamma - m\alpha_c)\alpha_c}{m - \gamma\alpha_c}\right]^{\frac{1}{2k_c}} . \tag{28}$$

Substituting Equation (28) into Equation (21) gives

$$\theta_{c,max} = -2\ln\left[\frac{m-\gamma\alpha_c}{m(1-\alpha_c^2)} z_o^{1+k_c} + \frac{(\gamma - m\alpha_c)\alpha_c}{m(1-\alpha_c^2)} z_o^{1-k_c}\right] . \tag{29}$$

Consider the case when the inner and outer surfaces are at the same temperature, i.e., $\gamma = 1$. Table 1 gives the values of $\alpha_c, \delta_c, F_{z=m}, F_{z=1}, H_{z=m}, H_{z=1}, z_o$, and $\theta_{c,max}$, for various values of m.

SEMI-INFINITE SLAB LIMIT

From Table 1 it is seen that as $m \to 1$, α_c is finite and $k_c \to \infty$. Equations (23), (24), (26) and (29) give

$$\lim_{\substack{\gamma=1\\ m\to 1}} \frac{F_{z=m}}{F_{z=1}} = -1 \; ; \; \lim_{\substack{\gamma=1\\ m\to 1}} \theta_{c,max} = \ln \frac{(1+\alpha_{c,1})^2}{4\alpha_{c,1}} = 1.1864 \tag{30}$$

where $\alpha_{c,1}$ = 0.090776 is the root of Equation (20) when $\gamma = m = 1$. Equation (30) has the following physical interpretation. As $a \to b$, the cross-sectional area of the cylindrical shell subtended by a small enough angle measured from the axis, may be considered as part of the cross-sectional area of a semi-infinite slab of thickness $\frac{1}{2}(b-a)$. There is a symmetric temperature distribution in the slab whose isothermal faces have equal temperature. Hence the fluxes at the surfaces are of equal magnitude but of opposite sign, showing that energy flows out from both faces. The dimensionless temperature at the center of the slab* is a maximum and equal to 1.1864.

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* For a slab of thickness $2b$, Equation (3) is $\frac{d^2\theta}{dz^2} = -\delta \exp(\theta)$. Frank-Kamenetzky found the critical temperature distribution to be

$$\theta_c = \theta_{max} - 2 \ln \cosh \left[\left(\frac{\delta_s}{2}\right)^{\frac{1}{2}} z \exp\left(\tfrac{1}{2}\theta_{max}\right) \right], \tag{31}$$

where $\delta_s = 0.87846$, the maximum of

$$\delta = 2 \left[\cosh^{-1} \exp\left(\tfrac{1}{2}\theta_{max}\right) \right]^2 \exp(-\theta_{max}), \tag{32}$$

occurs at $\theta_{max} = 1.1864$ which is the root of

$$\left[\exp(\theta_{max}) - 1\right]^{\frac{1}{2}} \left[\cosh^{-1} \exp\left(\tfrac{1}{2}\theta_{max}\right)\right] \exp\left(-\tfrac{1}{2}\theta_{max}\right) = 1. \tag{33}$$

θ_{max} is the slab center temperature.

From Equations (20) and (30), Equation (33) may be obtained. Hence the temperature defined by Equation (30) does indeed correspond to the slab center temperature. The critical value of δ, δ_s, for the slab of thickness $\frac{1}{2}(b-a)$, can be obtained from Equation (4). This gives

$$\frac{\delta_s}{\lim\limits_{\substack{\gamma=1\\ m\to 1}} \delta_c} = \frac{\left(\frac{b-a}{2}\right)^2}{b^2} = \frac{(1-m)^2}{4} \tag{34}$$

Therefore one finds

$$\delta_s = \frac{2\alpha_{c,1}}{(1+\alpha_{c,1})^2}(\ln \alpha_{c,1})^2 = 0.87846 \tag{35}$$

which has previously been found using Equation (32).

SOLID CYLINDER LIMIT

The solution for the solid cylinder can be shown to be a special case of the more general hollow cylinder solution. This is obtained by setting $D = 0$ in Equation (10) since the temperature gradient must vanish on the axis because of symmetry considerations. Therefore $\theta_m \neq 0$ at $m = 0$. From Equation (16)

$$\delta_c = 2 \;;\; A = \frac{1}{2}, \tag{36}$$

so that from Equation (14),

$$\theta_c = \ln 4 - 2\ln(z^2+1)\,;\; \theta_{c,max} = \ln 4 \tag{37}$$

These results for δ_c, θ_c, and $\theta_{c,max}$, are indentical with Chambré's.

ENGINEERING APPLICATIONS

Of late there has been a trend toward the design of large rocket grains. This trend toward larger types has made it necessary to determine how large a grain can be made before it presents a spontaneous ignition hazard. It is unfortunate that all the necessary physical constants needed for this determination are available for only a very few propellants or explosives.

A sample calculation of the critical size of cordite propellant for surface temperature at 300°K and 339°K (150°F) is given. The numerical constants for cordite[3] are as follows:

$E = 50{,}000$ cal mole^{-1}, $Z = 10^{21.8}$ sec^{-1}, $Q = 770$ cal cm^{-3}, and $\lambda = 5.3 \times 10^{-4}$ cal cm^{-1} sec^{-1} deg^{-1}. Table 2 gives the critical radius b (in meters) which corresponds to these two temperatures for various values of m (inner/outer diameter).

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m	α_c	δ_c	$F_{z=m}$	$H_{z=m}$	$-F_{z=1}, H_{z=1}$	Z_0	$\theta_{c,max}$
.010	.0039003	2.761	40.877	.4087	2.5298	.309503	1.22614
.020	.0074372	2.933	25.263	.5052	2.6423	.338881	1.21862
.030	.0107552	3.073	19.466	.5840	2.7319	.360008	1.21410
.040	.0138986	3.200	16.372	.6548	2.8111	.377325	1.21086
.050	.0168920	3.320	14.428	.7214	2.8846	.392378	1.20837
.060	.0197519	3.436	13.090	.7854	2.9544	.405909	1.20635
.070	.0224905	3.550	12.111	.8478	3.0219	.418335	1.20466
.080	.0251172	3.664	11.366	.9092	3.0879	.429917	1.20322
.090	.0276398	3.777	10.780	.9702	3.1530	.440831	1.20197
.100	.0300646	3.892	10.310	1.0310	3.2174	.451200	1.20087
.110	.0323975	4.007	9.926	1.0919	3.2816	.461116	1.19989
.120	.0346432	4.125	9.609	1.1531	3.3459	.470647	1.19901
.130	.0368061	4.245	9.344	1.2147	3.4103	.479848	1.19822
.140	.0388902	4.367	9.121	1.2769	3.4751	.488761	1.19750
.150	.0408990	4.492	8.932	1.3398	3.5404	.497420	1.19685
.160	.0428360	4.620	8.772	1.4036	3.6064	.505855	1.19625
.170	.0447040	4.752	8.636	1.4682	3.6732	.514089	1.19569
.180	.0465059	4.887	8.521	1.5339	3.7408	.522142	1.19518
.190	.0482444	5.027	8.424	1.6007	3.8094	.530030	1.19471
.200	.0499219	5.171	8.343	1.6687	3.8792	.537770	1.19427
.210	.0515408	5.319	8.275	1.7379	3.9500	.545372	1.19386
.220	.0531032	5.473	8.220	1.8085	4.0222	.552849	1.19348
.230	.0546112	5.631	8.176	1.8806	4.0957	.560209	1.19312
.240	.0560668	5.796	8.142	1.9542	4.1707	.567462	1.19278
.250	.0574718	5.966	8.118	2.0295	4.2473	.574615	1.19247
.260	.0588280	6.143	8.101	2.1064	4.3254	.581675	1.19216
.270	.0601372	6.326	8.093	2.1852	4.4054	.588647	1.19190
.280	.0614008	6.517	8.092	2.2658	4.4871	.595537	1.19163
.290	.0626206	6.715	8.098	2.3485	4.5708	.602351	1.19139
.300	.0637979	6.921	8.110	2.4332	4.6566	.609092	1.19115
.310	.0649342	7.136	8.129	2.5201	4.7445	.615765	1.19093
.320	.0660309	7.359	8.154	2.6094	4.8347	.622373	1.19072
.330	.0670892	7.593	8.185	2.7011	4.9272	.628920	1.19052
.340	.0681104	7.837	8.221	2.7953	5.0223	.635409	1.19033
.350	.0690957	8.091	8.263	2.8923	5.1200	.641843	1.19016
.360	.0700463	8.358	8.311	2.9920	5.2205	.648224	1.18999
.370	.0709632	8.636	8.364	3.0947	5.3239	.654555	1.18983
.380	.0718477	8.928	8.422	3.2005	5.4304	.660837	1.18967
.390	.0727006	9.234	8.486	3.3096	5.5402	.667074	1.18953
.400	.0735231	9.556	8.555	3.4222	5.6533	.673268	1.18939
.410	.0743160	9.893	8.630	3.5384	5.7701	.679419	1.18926
.420	.0750803	10.246	8.710	3.6584	5.8907	.685529	1.18913
.430	.0758169	10.621	8.796	3.7824	6.0153	.691601	1.18901
.440	.0765267	11.014	8.888	3.9107	6.1441	.697636	1.18890
.450	.0772105	11.426	8.985	4.0435	6.2774	.703635	1.18879
.460	.0778690	11.865	9.089	4.1810	6.4154	.709599	1.18868
.470	.0785031	12.328	9.199	4.3236	6.5584	.715530	1.18859
.480	.0791136	12.816	9.315	4.4715	6.7067	.721429	1.18849
.490	.0797011	13.334	9.438	4.6250	6.8607	.727296	1.18840
.500	.0802664	13.882	9.569	4.7845	7.0206	.733134	1.18832
.510	.0808102	14.465	9.706	4.9503	7.1868	.738943	1.18823
.520	.0813330	15.083	9.851	5.1230	7.3598	.744723	1.18815
.530	.0818356	15.742	10.005	5.3028	7.5399	.750476	1.18808
.540	.0823185	16.443	10.167	5.4903	7.7278	.756203	1.18801
.550	.0827824	17.192	10.338	5.6859	7.9237	.761904	1.18794
.560	.0832278	17.992	10.518	5.8903	8.1284	.767581	1.18788
.570	.0836553	18.848	10.709	6.1041	8.3425	.773233	1.18782
.580	.0840655	19.766	10.910	6.3279	8.5666	.778862	1.18776
.590	.0844588	20.752	11.122	6.5624	8.8014	.784468	1.18770
.600	.0848357	21.812	11.347	6.8086	9.0478	.790052	1.18765
.610	.0851968	22.955	11.585	7.0672	9.3066	.795614	1.18759
.620	.0855425	24.189	11.837	7.3393	9.5790	.801155	1.18755
.630	.0858732	25.524	12.104	7.6259	9.8658	.806676	1.18750
.640	.0861896	26.972	12.388	7.9283	10.1684	.812177	1.18746
.650	.0864918	28.545	12.689	8.2479	10.4882	.817658	1.18741
.660	.0867805	30.259	13.009	8.5860	10.8265	.823121	1.18737
.670	.0870559	32.131	13.350	8.9446	11.1853	.828564	1.18734
.680	.0873185	34.181	13.713	9.3254	11.5662	.833990	1.18730
.690	.0875686	36.432	14.102	9.7306	11.9716	.839398	1.18727
.700	.0878067	38.912	14.518	10.1626	12.4038	.844789	1.18723
.710	.0880331	41.653	14.963	10.6243	12.8656	.850163	1.18720
.720	.0882480	44.692	15.442	11.1188	13.3603	.855520	1.18717
.730	.0884520	48.075	15.958	11.6498	13.8914	.860862	1.18715
.740	.0886452	51.856	16.515	12.2214	14.4631	.866167	1.18712
.750	.0888280	56.099	17.118	12.8386	15.0805	.871497	1.18710
.760	.0890008	60.883	17.772	13.5071	15.7491	.876792	1.18707
.770	.0891637	66.304	18.485	14.2335	16.4756	.882072	1.18705
.780	.0893172	72.482	19.263	15.0258	17.2680	.887338	1.18703
.790	.0894614	79.562	20.118	15.8934	18.1356	.892589	1.18701
.800	.0895967	87.730	21.059	16.8475	19.0898	.897826	1.18699
.810	.0897233	97.222	22.101	17.9018	20.1442	.903050	1.18698
.820	.0898414	108.339	23.259	19.0731	21.3156	.908260	1.18696
.830	.0899514	121.474	24.556	20.3819	22.6245	.913457	1.18695
.840	.0900534	137.149	26.016	21.8542	24.0968	.918641	1.18693
.850	.0901477	156.061	27.673	23.5225	25.7652	.923812	1.18692
.860	.0902346	179.169	29.568	25.4288	27.6716	.928971	1.18691
.870	.0903141	207.812	31.756	27.6283	29.8710	.934118	1.18690
.880	.0903866	243.911	34.311	30.1939	32.4368	.939252	1.18689
.890	.0904523	290.295	37.332	33.2258	35.4687	.944375	1.18688
.900	.0905113	351.280	40.959	36.8637	39.1066	.949486	1.18687
.910	.0905638	433.704	45.595	41.3097	43.5527	.954586	1.18687
.920	.0906102	548.936	50.942	46.8668	49.1098	.959675	1.18686
.930	.0906504	717.009	58.076	54.0112	56.2542	.964752	1.18685
.940	.0906847	975.966	67.592	63.5365	65.7795	.969819	1.18685
.950	.0907133	1405.436	80.917	76.8713	79.1144	.974875	1.18685
.960	.0907364	2196.051	100.909	96.8728	99.1159	.979920	1.18684
.970	.0907540	3904.168	134.234	130.2077	132.4507	.984955	1.18684
.980	.0907665	8784.514	200.893	196.8760	199.1190	.989980	1.18684
.990	.0907738	35138.465	400.887	396.8786	399.1217	.994995	1.18684
1.000	.0907762	∞	∞	∞	∞	1.000000	1.18684

TABLE I VALUES OF $\alpha_c, \delta_c, F_{z=m}, F_{z=1}, H_{z=m}, H_{z=1}, Z_0$, AND $\theta_{c,max}$.

FOR DIFFERENT m WHEN $\gamma = 1$

TABLE 2 VALUES OF b (IN METERS) FOR DIFFERENT VALUES OF m AND T_b

T_b \ m	S.C.*	0.01	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
300°K	168	197	234	270	312	367	442	554	740	1,112	2,222
339°K	1.41	1.65	1.96	2.26	2.62	3.08	3.70	4.65	6.21	9.33	18.64

* Solid Cylinder

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